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<b>(21) International Application Number:</b> PCT/US98/15267  <b>(22) International Filing Date:</b> 21 July 1998 (21.07.98)  <b>(30) Priority Data:</b> 60/053,332      21 July 1997 (21.07.97)      US  <b>(71)(72) Applicant and Inventor:</b> FRUCI, Vittoria [US/US]; 117 Ontario Street #2, Lockport, NY 14094 (US).  <b>(74) Agents:</b> ROGALSKYJ, Peter et al.; Nixon, Hargrave, Devans & Doyle LLP, Clinton Square, P.O. Box 1051, Rochester, NY 14603 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title: METHOD FOR PREPARING SILICONE POLYMERS</b>		
<b>(57) Abstract</b>  <p>The present invention relates to a method for producing a silicone polymeric composition having an adhesive surface or a drag reducing surface. The surface of a silicone polymer precursor is contacted with a cross-linking inhibitor and is optionally agitated to cause the cross-linking inhibitor to mix with the silicone polymer precursor's surface. By polymerizing and curing the silicone polymer precursor under conditions which are effective to polymerize and cross-link the silicone polymer precursor without cross-linking the surface of the silicone polymer precursor contacted with the cross-linking inhibitor, a silicone polymeric composition having an adhesive and drag-reducing surface is produced. Methods for attaching a medical implant to a biological material and for reducing boat hull drag are also disclosed. The medical device or boat hull is coated with a silicone polymer precursor, which is then contacted with a cross-linking inhibitor, the silicone polymer precursor coating's surface is contacted with a cross-linking inhibitor, and the silicone polymer precursor coating is polymerized and cured under conditions which are effective to polymerize and cross-link the silicone polymer precursor without cross-linking the surface of the silicone polymer precursor contacted with the cross-linking inhibitor.</p>		

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## METHOD FOR PREPARING SILICONE POLYMERS

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The Federal Government may retain certain rights in the  
invention.

FIELD OF INVENTION

10 The present invention relates, generally, to  
methods for preparing silicone polymer compositions and,  
more particularly, to methods for preparing silicone  
polymer compositions having adhesive and drag-reducing  
15 surfaces.

BACKGROUND OF THE INVENTION

20 Various coatings have been developed for  
reducing drag between two surfaces in relative motion.  
For example, U.S. Patent No. 2,937,976 to Granahan uses a  
drag reducing gel for a razor blade and U.S. Patent No.  
4,385,134 to Foscante teaches use of a drag-reducing,  
antifouling coating for boat hulls.

25 The primary cause of drag on boat hulls is the  
growth of marine organisms on the hull. Generally,  
antifouling coatings contain a toxicant agent which  
controls the growth of marine organisms. When using such  
coatings it is necessary to control the amount of toxin  
30 delivered to the coating's surface in order to prevent  
premature depletion of the antifouling agent. This  
control is frequently difficult to achieve.

35 A need continues to exist for a method of  
reducing drag which is easy to carry out, which can be  
used for pre-existing objects, and which imparts to the  
object long-lasting resistance to oxidation, water  
seepage, bacterial degradation, and the like. The

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present invention is directed, in part, to meeting this need.

Prosthetic devices are widely employed for functional or cosmetic purposes to correct congenital, developmental, or acquired defect. Since facial appearance and expression are both highly visible, defects of the head and neck areas come under closer scrutiny than defects of other body parts. Therefore, preparation of maxillofacial prosthetics requires the use of both art and science to reconstruct defects.

There are two general categories of maxillofacial prosthetics, namely, intraoral and extraoral. Intraoral prostheses are usually fabricated in association with a partial or complete denture. Retention of intraoral prostheses usually pose few problems except in a completely edentulous patient having markedly resorbed ridges, poor quality bony or soft tissue undercuts, and a bulky or weighty obturator. Extraoral prostheses pose more retentive as well as aesthetic problems. A major disadvantage for a patient wearing an extraoral prosthetic device is the potential for dislodgement during normal activity and the accompanying patient embarrassment.

A number of different types of polymeric materials have been utilized as base materials for prostheses. Principal among these polymers have been the silicone rubbers and polyurethanes. These elastomeric polymers are used for most extraoral prostheses because of the life-like qualities that can be imparted to them. These qualities include flexibility and the ability to be colored. This coloring is accomplished by adding fibers or pigment to the prepolymer or by tattooing the completed prostheses to conform them closely to the skin tones of the areas contiguous to the reconstructive site.

The chemical inertness of these polymers, once cured, is a major factor in their popularity for maxillofacial prosthetic reconstruction. However, the same chemical inertness and inherently non-stick

properties which makes polymers, such as silicone rubbers, desirable prosthetic materials also is the cause of the majority of difficulties in working with them. While, in some cases, the use of surgery to provide tissue undercuts to aid in mechanically retaining a prosthesis is possible, in many other cases adhesives alone, or in combination with other mechanical retention aids, such as wires, elastics, or eyeglasses, must be used as the primary means for retention. For example, a prosthetic ear may have virtually no means for retention other than an adhesive. This is also true in most cases where the defect is large or cannot be surgically modified to provide mechanical retention.

Not only must the adhesive hold the prosthesis in place, it must also permit regular removal and reattachment for hygienic purposes, such as to clean the prosthesis or the surrounding and underlying tissue. Significant effort has been expended in developing satisfactory and medically safe adhesives for routinely detaching and re-securing prosthetic devices. The problems associated with applying adhesives to and retaining them on inherently non-stick surfaces, such as silicone rubber, are readily apparent. These problems are compounded by the presence of surface contaminants such as dirt, oils, and dead skin on the tissue to which the prosthetic device is to be applied. Once cured, many adhesives no longer are sticky and will not bond again after removal. Also, many adhesives that have pressure sensitive properties lose their adherent properties once their surface has been contaminated.

Accordingly, the need exists in the art for methods of preparing medically acceptable polymer compositions suitable for use as prosthetic device adhesives which possess permanently adherent properties and which can be repetitively applied and detached from human skin or other surfaces. The present invention is, in part, directed to meeting this need.

SUMMARY OF THE INVENTION

The present invention relates to a method for producing a silicone polymeric composition having an adhesive surface. A silicone polymer precursor is provided, and the silicone polymer precursor's surface is contacted with a cross-linking inhibitor. The silicone polymer precursor's surface is agitated under conditions effective to cause the cross-linking inhibitor to mix with the silicone polymer precursor's surface. The silicone polymer precursor is polymerized and cured under conditions which are effective to polymerize and cross-link the silicone polymer precursor without cross-linking the surface of the silicone polymer precursor contacted with the cross-linking inhibitor. In this manner, a silicone polymeric composition having an adhesive surface is produced.

The present invention also relates to a method for attaching a medical implant to a biological material. The implant is coated with a silicone polymer precursor to form a coating on the implant, and the silicone polymer precursor coating's surface is contacted with a cross-linking inhibitor and agitated under conditions effective to cause the cross-linking inhibitor to mix with the silicone polymer precursor coatings's surface. By polymerizing and curing the silicone polymer precursor coating under conditions effective to polymerize and cross-link the silicone polymer precursor coating without cross-linking the surface of the silicone polymer precursor coating contacted with the cross-linking inhibitor, a coated implant having an adhesive surface is formed. The adhesive surface of the coated implant is then contacted with the biological material under conditions effective to attach the medical implant to the biological material.

In another aspect, the present invention relates to a method for producing a silicone polymeric composition having a drag-reducing surface. The surface

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of a silicone polymer precursor is contacted with a cross-linking inhibitor, and the silicone polymer precursor's surface is agitated under conditions effective to cause the cross-linking inhibitor to mix  
5 with the silicone polymer precursor's surface. The silicone polymer precursor is polymerized and cured under conditions effective to polymerize and cross-link the silicone polymer precursor without cross-link the surface of the silicone polymer precursor. In this manner, a  
10 silicone polymeric composition having a drag-reducing surface is produced.

In yet another aspect, the present invention relates to a method for reducing boat hull drag. The method includes coating the boat hull with a silicone  
15 polymer precursor and contacting the silicone polymer precursor coating's surface with a cross-linking inhibitor. By polymerizing and curing the silicone polymer precursor coating under conditions effective to polymerize and cross-link the silicone polymer precursor  
20 coating without cross-linking the surface of the silicone polymer precursor coating contacted with the cross-linking inhibitor, the boat hull's drag is reduced.

The present invention provides a convenient method for producing silicone or silicone-coated  
25 materials having uncured surfaces. These uncured surfaces make the materials attractive for a number of applications. In particular, the method permits creation of an adhesive surface on the atmosphere-to-sample side of a silicone polymer rather than on the mold-to-polymer  
30 side and permits the creation of adhesive surfaces on silicone objects which are shaped by methods other than molding processes, such as spin casting. Moreover, the methods do not require that the cross-linking inhibitor be incorporated in the silicone precursor prior to  
35 polymerization. Thus, the method offers greater control and flexibility in the application of the cross-linking inhibitor to the silicone material and permits the

efficient production of silicone or silicone-coated objects having a greater variety of sizes and shapes.

#### DETAILED DESCRIPTION OF THE INVENTION

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The present invention relates to a method for producing a silicone polymeric composition having an adhesive surface. A silicone polymer precursor is provided, and the silicone polymer precursor's surface is contacted with a cross-linking inhibitor. The silicone polymer precursor's surface is agitated under conditions effective to cause the cross-linking inhibitor to mix with the silicone polymer precursor's surface. The silicone polymer precursor is then polymerized and cured under conditions which are effective to polymerize and cross-link the silicone polymer precursor without cross-linking the surface of the silicone polymer precursor contacted with the cross-linking inhibitor. In this manner, a silicone polymeric composition having an adhesive surface is produced.

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The silicone polymeric precursor can be, for example, silicone monomers or silicone prepolymers, the latter of which includes partially polymerized silicone monomer (i.e., polymeric silicone units having reactive groups attached thereto capable of further polymerization) and fully or substantially fully polymerized silicone which is uncured and/or unvulcanized. The silicone polymer precursor can be precursors of polymeric silicone, or precursors of copolymers of silicone and other polymers, such as polyurethanes, polyacrylics, polyesters, polyolefins, polyacrylamides, and polyurethane.

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Silicone polymer precursors which are partially or substantially fully polymerized prior to their contact with the cross-linking inhibitor can be prepared by mixing silicone polymer precursor with a catalyst effective to polymerize some or substantially all of the silicone polymer precursor present. Suitable catalysts

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are selected based upon the nature of the silicone polymer precursor used. For example, where the silicone polymer precursor is a commercially available silicone precursor, suitable catalysts are provided along with the commercial silicone precursor. Suitable two-part commercially available silicone precursors include SILASTIC Medical Grade ETR Elastomers (e.g., Dow Corning Product Nos. Q7-4735, Q7-4750, and Q7-4765, and other products described in U.S. Patent No. 3,445,420 to Kookootsedes et al.), SILASTIC MDX-4-4210 Medical Grade Elastomer, SILGARD 194, and SILGARD 196, all available from Dow Corning Corp.; general purpose condensation cure silicones, such as RTV11, RTV12, RTV21, and RTV41; high temperature condensation cure silicones, such as RTV8111, RTV8112, RTV8262, RTV31, RTV60, RTV88, RTV560, and RTV566, and low temperature condensation cure silicones, such as RTV511, RTV567, and RTV577, all available from General Electric Co.; and general purpose addition cure silicones, such as RTV615, RTV627, RTV630, RTV6428, and TSE3033, thermally conductive addition cure silicones, such as TSE3320, TSE3331, and TSE3380, low temperature addition cure silicones, such as RTV656, and addition cure silicone gels, such as RTV6126, RTV6136, RTV6156, RTV6166, RTV6186, and RTV6196, all available from General Electric Co. The amount of catalyst employed is not critical to the practice of the present invention, but it is preferred that the amount of catalyst be sufficient to polymerize substantially all (such as greater than 90%) of the silicone polymer precursor present. For example, where MDX 4-4210 silicone polymer precursor is employed, one part of the catalyst is mixed with each 10 parts by weight of silicone polymer precursor. Typically, the catalyst employed for polymerization of the silicone polymer precursor is one capable of catalyzing a condensation reaction between silicone atoms which are typically bonded to one or more hydroxy or halogen substituents. The polymerization reaction can be carried out by heating

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the silicone polymer precursor to a temperature of from about 30°C to about 60°C for from about 5 hours to about 2 hours or at a temperature of from about 70°C to about 110°C for from about 30 minutes to about 15 minutes.

5 Polymerization can also be carried out at room temperature or even lower, but this takes appreciably more time (about 1 day or more).

One part silicones can also be used in the practice of the present invention. These include alkoxy-cured silicones, such as TRV5222, RTV5223, RTV5229, RTV5242, RTV5243, RTV5249, RTV160, RTV162, RTV167; acetoxycured silicones, such as RTV102, RTV103, RTV108, RTV109, IS802, IS803, IS808, RTV112, and RTV118; and high temperature or fuel resistant silicones, such as FRV1106, FRV1107, RTV1473, RTV133, RTV106, IS806, RTV116, RTV159, RTV142, and RTV157, all available from General Electric Co.

When the silicone polymer precursor is polymerized prior to its being contacted with the cross-linking inhibitor, polymerization is typically carried out after the silicone polymer precursor has been fabricated into a desired shape. A variety of different methods can be used to shape the silicone polymer precursor, including extrusion, spin-casting, calendaring, and molding techniques, such as injection molding. These and other techniques for shaping silicone products are described in, for example, Metevia et al., "Fabricating Silicone Rubber," in Hseih et al., eds., Controlled Release Systems: Fabrication Technology, Volume II, Boca Raton, Florida: CRC Press, pp. 111-136 (1988), which is hereby incorporated by reference. Alternatively, the silicone polymer precursor can have the form of a thin layer, such as one having a thickness of from about 0.1 mm to about 30 mm. Preferably, the thin layer forms a coating on a substrate made of, for example, paper, wood, fiberglass, plastic, metal, glass, and mixtures thereof. In addition to the aforementioned materials, the substrate can be made of cured silicone,

particularly where the substrate is a medical implant. Coating of the silicone polymer precursor onto the substrate can be achieved by a variety of different techniques, such as painting, dipping, sputtering, spraying, and the like.

In cases where the silicone polymer precursor is formed as a coating on a substrate, it is coated on the substrate prior to the introduction of the cross-linking inhibitor. The coating can be formed prior to, during, or after the silicone polymer precursor is polymerized. For example, silicone monomer can be coated on the substrate and then partially or fully or substantially fully polymerized prior to introducing the cross-linking inhibitor. Alternatively, the silicone monomer can be partially polymerized prior to coating the substrate. In this case, it is advantageous to coat the substrate with the silicone polymer precursor during the early stages of the polymerization process, because, during the later stages of the polymerization process, the silicone polymer precursor may become too viscous to form a uniformly thick coating on the substrate. After coating the partially polymerized silicone polymer precursor on the substrate, the partially polymerized silicone polymer precursor can be allowed to further polymerize prior to contacting it with the cross-linking inhibitor.

As indicated above, the polymerization process, whether conducted prior to or after coating the silicone polymer precursor on a substrate, is carried out under conditions which are effective to polymerize the silicone polymer precursor to form an polymerized silicone material. However, these conditions are preferably ineffective to cure the polymerized silicone polymer precursor. In this regard, it is believed that cured silicone polymer is formed by a two step process: a relatively fast polymerization step in which the terminal groups of the silicone polymer precursor react together to form long linear chains of polymerized silicone; and a

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second, relatively slower step in which the long chains of polymerized silicone are cross-linked in a process known as curing. Polymerized silicone polymer is characterized by its increased viscosity relative to the monomeric precursor but lacks the cross-links which make cured silicone resilient.

After providing the silicone polymer precursor, and optionally coating it on a substrate, the surface of the silicone polymer precursor is contacted with a cross-linking inhibitor.

Suitable cross-linking inhibitors include carboxylic acids, particularly carboxylic acids having the formula  $R-COOH$ , where  $R$  represents a substituted or unsubstituted  $C1-C12$  branched, cyclic, or linear alkyl or  $C6-C18$  aryl group, such as acetic acid, propionic acid, and the like, metal salts of carboxylic acids, such as stannous octonate, chlorinated and butyl rubbers, sulfur containing solvents, plasticizer, tin containing compounds, oxidizing oils, linseed oils, putties, oils containing clays, and amine-containing plasticizers. The particular cross-linking inhibitor used depends, in part, on the nature of the silicone polymer precursor employed. For example, silicone polymer precursors, such as MDX 4-4210, SILGARD 184 and 186, and SILASTIC 31-10, 31-12, and 31-20, are particularly compatible with inhibitors, such as chlorinated and butyl rubbers, sulfur containing solvents, plasticizer containing compounds, and tin containing compounds. Silicone polymer precursors, such as SILASTIC 382 and GE RTV-11, are compatible with inhibitors, such as the aforementioned oils as well as plasticizers, specifically amine containing plasticizers.

One particularly useful cross-linking inhibitor is a ketone. The ketone is preferably provided in the form of a liquid, and, for example, can be acetone, methyl ethyl ketone, diethyl ketone, or combinations thereof. It is particularly preferred to use a cross-linking inhibitor which includes acetone and one or more of the following: water, an amine salt of a fatty acid

amide of a hydrolyzed collagen, and an acid addition salt of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant. More preferably, the cross-linking inhibitor includes from about 70 to about 90 wt% acetone, from about 5 to about 17 wt% water, from about 0.01 to about 0.15 wt% of an amine salt of a fatty acid amide of a hydrolyzed collagen, and from about 0.1 to about 0.8 wt% of an acid addition salt of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant. Suitable amine salts of a fatty acid amide of a hydrolyzed collagen include the aminomethylpropanol salt of the isostearic amide of hydrolyzed collagen, and suitable acid addition salts of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant include cocamidopropyl dimethylaminopropionate. Other suitable amine salts of a fatty acid amide of a hydrolyzed collagen and acid addition salts of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant include those described in U.S. Patent No. 4,485,037 to Curtis ("Curtis"), which is hereby incorporated by reference. These formulations are commonly used in nail polish removers and can be purchased commercially or can be prepared in accordance with Curtis, which is hereby incorporated by reference.

The cross-linking inhibitor can be contacted with the silicone polymer precursor's surface directly or indirectly. By indirectly, it is meant that the cross-linking inhibitor is first applied to an inert substrate which is then contacted with the silicone polymer precursor surface. For example, the cross-linking inhibitor, such as a ketone or a composition which includes a ketone, can be applied to the surface of a mold, and the silicone polymer precursor can then be pressed into the mold so that the silicone polymer precursor's surface comes into contact with the cross-linking inhibitor on the mold's surface. Alternatively and preferably, the cross-linking inhibitor is applied directly to the silicone polymer precursor's surface,

such as by painting, spraying, sputtering, dipping, and the like, without first applying it to an inert substrate. For example, a ketone-containing cross-linking inhibiting composition can be painted, such as with a brush or a roller, on the silicone polymer precursor's surface.

After this contacting is carried out, it is advantageous, but not necessary, to agitate the silicone polymer precursor's surface under conditions effective to mix the cross-linking inhibitor with the silicone polymer precursor's surface. This agitation can be effected in a number of ways, such as by the use of brushes, rollers, spatulas, and the like. In a preferred embodiment, subsequent to applying a ketone-containing cross-linking inhibitor with a brush, brushing of the silicone polymer precursor's surface is continued for a period of time, preferably from about 1 minute to about 1 hour, to effect agitation. By varying the duration, vigorousness, and tool used to carry out agitation, the depth to which the cross-linking inhibitor mixes with the silicone polymer precursor's surface can be controlled. Preferably, agitation mixes the cross-linking inhibitor with the silicone polymer precursor's surface to a depth of from about 0.01 mm to about 25 mm, depending on the thickness of the silicone polymer precursor. Typically, agitation is effective to mix the cross-linking inhibitor with the silicone polymer precursor's surface to a depth of from about 10% to about 50% of the thickness of the silicone polymer precursor.

After contacting the silicone polymer precursor's surface with the cross-linking inhibitor and, optionally, agitating, the silicone polymer precursor is polymerized and cured.

In the case where the silicone polymer precursor was partially polymerized prior to contacting its surface with the cross-linking inhibitor, polymerization and curing is simply a continuation of the polymerization process coupled with curing. In the case

where the silicone polymer precursor was unpolymerized, polymerization can be effected simply by the passage of time, or, alternatively, it can be accelerated by the presence of a catalyst, by the application of heat, or both using, for example, the methods and conditions described above for pre-polymerization.

The curing process, frequently referred to as vulcanization, can be carried out simply by the passage of time, or, alternatively, it can be accelerated by the application of, for example, heat. Generally, curing can be effected by exposing the silicone polymer precursor to: a temperature of from about 35 °C to about 45 °C for from about 4 hours to about 6 hours; a temperature of from about 50 °C to about 60 °C for from about 1 hour to about 3 hours; a temperature of from about 65 °C to about 85 °C for from about 15 minutes to about 1 hour; a temperature of from about 90 °C to about 110 °C for from about 5 minutes to about 30 minutes. Alternatively, curing can be carried out at room temperature in from about 12 hours to about 8 days, preferably from about 48 hours to about 8 days. During the curing process, the bulk of the silicone polymer precursor becomes cross-linked, but the surface of the silicone polymer precursor which had been contacted with the cross-linking inhibitor remains uncured. The non-cross-linked nature of the uncured surface imparts to that surface an adhesive quality which can be exploited in a variety of applications.

The adhesive silicone polymers can be used in any environment where self-adhesive cushioning materials are desired. For example, they can be used as furniture bumpers, as coatings for glass surfaces (e.g., windows and windshields), and as soft antiskid mats, such as for diaper changing stations and bathtubs. The adhesive silicone polymers of the present invention can also be used to reversibly adhere materials, such as artwork or advertisements, to vertical surfaces, such as walls, by applying sheets of the adhesive silicone polymer to the

vertical surface with the adhesive side out. The adhesive silicone polymers of the present invention can, alternatively, be used as a moisture and water resistant tape, such as for diapers or feminine hygiene products.

5 The adhesive silicone polymers can also be used to insulate glass and other surfaces, such as window panes and windshields, or to modify the surface energy of metals and other materials.

The method of the present invention can be advantageously used to attach a medical implant to a biological material. In this process, the implant is first coated with a silicone polymer precursor. The coated silicone polymer precursor coating has an exposed surface which is then contacted with a cross-linking inhibitor, such as those described above, particularly a ketone or a composition containing a ketone. The silicone polymer precursor coating's surface can be, but need not be, agitated to mix the cross-linking inhibitor with the silicone polymer precursor coating's surface to a desired depth. In this way the depth to which the silicone polymer precursor coating will remain uncured can be controlled. The silicone polymer precursor coating is then polymerized and cured under conditions effective to polymerize and cross-link the silicone polymer precursor coating. Conditions suitable for polymerizing and curing the silicone polymer precursor include those which were discussed above. The surface of the silicone polymer precursor coating in contact with the cross-linking inhibitor remains uncured, which imparts to it an adhesive character. The adhesive surface of the coated implant is then contacted with a biological material under conditions effective to attach the medical implant to the biological material. For example, the adhesive surface of the coated implant can simply be pressed against the biological material for a period of time, typically from about 30 seconds to about 5 minutes, after which the adhesive surface of the coated implant remains attached to the biological material



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without further pressure. Optionally, other medically-acceptable adhesives, such as dental adhesives, bone cement, tooth surface cement, tissue bonding cement; mechanical fasteners, such as screws, staples, or sutures; or combinations of these can be used in conjunction with the methods of the present invention.

Using the above method of the present invention, a wide variety of medical implants, such as prosthetic appliances, teeth, synthetic blood vessels (adhesive side on the exterior surface thereof), drug-releasing patches, and the like, can be attached to biological materials. As used herein, drug-releasing patches are meant to include those which sustainedly release hormones, steroids (including contraceptive steroids), aspirin, anti-cancer agents, nicotine, and anti-inflammatories, as well as other agents described in Kydonieus, ed., Controlled Release Technologies: Methods, Theories, and Applications, Volume II, Boca Raton, Florida: CRC Press (1980) ("Kydonieus") and Wise, ed., Biopolymeric Controlled Release Systems, Volume II, Boca Raton, Florida: CRC Press (1984), which is hereby incorporated by reference. Other implants which can be made self-adhering by the method of the present invention include monitoring devices, such as those used to continuously monitor pulse, blood pressure, temperature, electrocardio activity, brain activity, and/or blood flow. These implants can be made of cured silicone or of any material which is well suited for the function of the implant, such as plastics, fiberglass, metal, ceramics, and glass.

As used herein, biological materials include, for example, skin, particularly human skin, bones, teeth, and the like.

The adhesive silicone polymers of the present invention can also be used to sustainedly deliver cleansing, antibacterial, or other materials in the same manner that conventional silicone polymers are used to release these materials in a controlled manner. For

example, the adhesive silicone polymers of the present invention can contain an antibacterial, antifungal, antiviral, or antimildew agent which is sustainedly released therefrom. These materials are especially  
5 useful when adhered to surfaces where bacterial, fungal, viral, and/or mildew growth is particularly undesirable or likely. Such surfaces include sinks and cutting surfaces in the meat cutting and packing industries, public shower and bathroom surfaces, floors, and baby  
10 changing stations. The adhesive silicone polymers of the present invention can also be used to make preformed bathtub caulk (adhesive side applied toward wall), bathtub mats (adhesive side toward tub), pool liners (adhesive side down), and cushioning liners for sinks and  
15 floors (adhesive side down). In each of these products, it is particularly advantageous to incorporate into silicone polymer one or more sustainedly releasable cleansing, antibacterial, antifungal, antiviral, or antimildew agents.

20 The present invention, in another aspect thereof, relates to a method for producing a silicone polymeric composition having a drag-reducing surface. As used herein, drag relates to the friction experienced by a body moving relative to, such as through, a fluid  
25 medium, particularly water or other aqueous medium.

The silicone polymeric composition having a drag reducing surface is prepared by contacting a silicone polymer precursor with a cross-linking inhibitor. The silicone polymer precursor's surface is  
30 optionally agitated under conditions effective to cause the cross-linking inhibitor to mix with the silicone polymer precursor's surface. The silicone polymer precursor is then polymerized and cured under conditions which are effective to polymerize and cross-link the  
35 silicone polymer precursor without cross-linking the surface of the silicone polymer precursor contacted with the cross-linking inhibitor. In this manner, a silicone

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polymeric composition having drag-reducing surface is produced.

5           Suitable silicone polymer precursors, cross-linking agents, and reaction conditions are the same as those specified above with regard to the method of producing a silicone polymeric composition having an adhesive surface of the present invention.

10           In particular, the methods of the present invention can be used to reduce the drag experienced by objects, particularly boat hulls, as they move through water or other aqueous media. The method includes coating the boat hull with a silicone polymer precursor. Suitable silicone polymer precursors include those described above with respect to methods for producing  
15           silicone polymeric compositions having adhesive surfaces. The boat hull can be coated by any conventional method, such as spraying, painting, sputtering, and the like. The silicone polymer precursor coating's surface is then contacted with a cross-linking inhibitor, such as those  
20           described above, particularly a ketone or a ketone-containing composition, such as, for example, those described in Curtis, which is hereby incorporated by reference. Following an optional agitation of the silicone polymer precursor coating's surface to mix the  
25           cross-linking agent with the with the silicone polymer precursor coating, the silicone polymer precursor coating is polymerized and cured under conditions effective to polymerize and cross-link the silicone polymer precursor coating. Catalysts suitable for polymerizing and curing  
30           the silicone polymer precursor coating, as well as the conditions under which polymerization and curing can be effectively carried out include those specified above with regard to producing silicone polymeric compositions having adhesive surfaces.

35           The surface of the silicone polymer precursor coating which had been contacted with the cross-linking inhibitor remains non-cross-linked, thus producing a boat hull which exhibits reduced drag. Although, the

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mechanism by which the absence of surface cross-linking of silicone polymers reduces drag is not well understood, it has been observed that these uncured (i.e., non-cross-linked) surfaces, when moving through an aqueous medium, experience reduced drag. For example, see U.S. Patent No. 4,839,456 to Kent, which is hereby incorporated by reference.

The silicone polymers of the present invention can also be used to reduce drag in other environments, such as the inside walls of pipes and ductwork. Illustrative examples of pipes and ductwork include those used in power plant heat exchangers, condensers, and intake lines, municipal and biological water supply lines, cooling circuits in oil refineries, sewage conduits, and catheters (e.g., those used for angiography or to deliver liquid to any internal organ or cavity). The silicone polymer precursor can be applied to the inside walls of pipes or ductwork and subsequently treated with a cross-linking inhibitor in a manner analogous to the process used to coat boat hulls, described above.

In many situations, such as where the pipes or ductwork are used in transporting food products (e.g., milk and dairy products, particularly in the pasteurization thereof, beverages, canned goods, sugars, syrups, meats, fats, and beer, particularly in the fermentation thereof) or air (e.g., air ducts in heating, air-conditioning, and ventilation systems in cars, homes, offices, and the like), the silicone polymers can contain an agent which is sustainedly released to control, for example, fungal and bacterial growth. Particular agents for sustained release in these situations include, for example, antibacterial agents, antifungal agents, and combinations thereof. Further details regarding the incorporation of such agents in silicone materials can be found, for example, in Kydonieus, which are hereby incorporated by reference.

The present invention is further illustrated by the following examples.

#### EXAMPLES

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##### Example 1

Silicone polymer precursor designated MDX4-4210, commercially available from Dow Corning Corp., Midland, Michigan, was prepared. Acetone-based and acetic acid-based cross-linking inhibitor agents were separately applied to selected atmosphere-to-precursor surfaces of the polymer. The surfaces where the inhibiting agents were applied were agitated to a depth of about 1-3 mm to thoroughly mix precursor and inhibitor until a change in consistency was noted. In some samples, agitation was performed at multiple times during the curing process including at the time of precursor preparation and up to approximately 2-3 hours into curing. In other samples, agitation was performed once either at the time of precursor preparation or at some time during the curing process up to approximately 2-3 hours into curing. The polymer was allowed to cure at room temperature for approximately 72 hours, or the polymer was heated at 100-150°F for approximately 2 hours. After complete curing, the surfaces of the polymer in contact with the cross-linking inhibitor agents were tacky and exhibited pressure sensitive adhesive properties.

##### Example 2

Silicone polymer precursor mentioned in Example 1 was spread on to a previously cured sample of the same silicone precursor. The same inhibitors as in Example 1 were separately added to the uncured atmosphere-to-precursor surfaces and agitated to thoroughly mix the uncured precursor and the inhibitor. This mixture was cured at room temperature for approximately 72 hours. Upon curing the polymer surfaces in contact with the cross-linking inhibitors were tacky and exhibited pressure sensitive adhesive properties.

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Example 3

GE RTV11 polymer, commercially available from General Electric Company, Poestenkill, New York, was prepared. The same inhibitors as in Example 1 were separately applied to selected atmosphere-to-precursor surfaces of the polymer. The area was agitated and the polymer was allowed to cure at room temperature for approximately 24 hours. Upon curing, the polymer surfaces in contact with the cross-linking inhibitors were tacky and exhibited pressure sensitive adhesive properties.

Example 4 -- Testing

Multiple Attenuated Internal Reflection Infrared ("MAIR-IR") spectra were obtained of the acetone and acetic acid based inhibitor tacky samples (in Example 1) as well as the corresponding non-tacky samples (i.e., samples that were not treated with inhibitor). Spectra were also obtained for residues of each sample (i.e., remnants of the samples remaining on the prism after obtaining the MAIR-IR spectrum and removing the sample from the prism). All spectra showed silicone signatures with no differences between the tacky versus the non-tacky surfaces. The residues of each sample showed less proportions of the same silicone peaks. Spectra were also obtained of the acetone based inhibitor (in Example 1). These spectra showed peaks of typical hydrocarbon and alcohol residues.

Non-polarized photographs of the acetone and acetic acid based inhibited tacky surfaces and non-tacky surfaces magnified 100X on a light microscope were obtained. No differences between the tacky versus the non-tacky samples or the acetone versus the acetic acid based inhibitor samples were noted. The photographs had no distinguishing characters between them.

Although the invention has been described in detail for the purpose of illustration, it is understood that such detail is solely for that purpose, and variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention which is defined by the following claims.

## WHAT IS CLAIMED:

1. A method for producing a silicone polymeric composition having an adhesive surface comprising:

providing a silicone polymer precursor having a surface;

contacting the silicone polymer precursor's surface with a cross-linking inhibitor;

agitating the silicone polymer precursor's surface under conditions effective to cause the cross-linking inhibitor to mix with the silicone polymer precursor's surface; and

polymerizing and curing the silicone polymer precursor under conditions effective to polymerize and cross-link the silicone polymer precursor without cross-linking the surface of the silicone polymer precursor contacted with the cross-linking inhibitor, whereby a silicone polymeric composition having an adhesive surface is produced.

2. A method according to claim 1, wherein the cross-linking inhibitor is selected from the group consisting of ketones, carboxylic acids, metal salts of carboxylic acids, chlorinated rubbers, butyl rubbers, room-temperature vulcanizing silicone rubbers, sulphur-containing solvents, plasticizers, tin-containing compounds, oxidizing oils, and combinations thereof.

3. A method according to claim 1 further comprising:

coating a substrate with the silicone polymer precursor prior to said contacting.

4. A method according to claim 3, wherein the substrate is a medical implant.

5. A method according to claim 3, wherein the silicone polymer precursor forms a coating having a thickness of from about 0.1 mm to about 30 mm on the substrate.

6. A method according to claim 3, wherein the substrate is made of a material selected from the group consisting of paper, wood, fiberglass, plastic, metal, glass, and mixtures thereof.

7. A method according to claim 3, wherein the substrate is made of cured silicone.

8. A method according to claim 1, wherein the silicone polymer precursor has a thickness and wherein said agitating mixes the cross-linking inhibitor with the silicone polymer precursor's surface to a depth of from about 10% to about 50% of the thickness of the silicone polymer precursor.

9. A method according to claim 1, wherein said contacting the silicone polymer precursor's surface with a cross-linking inhibitor comprises:

applying the cross-linking inhibitor directly to the silicone polymer precursor's surface.

10. A method for attaching a medical implant to a biological material comprising:

coating the implant with a silicone polymer precursor, wherein the silicone polymer precursor forms a coating on the implant, said coating having a surface;

contacting the silicone polymer precursor coating's surface with a cross-linking inhibitor;

agitating the silicone polymer precursor coating's surface under conditions effective to cause the cross-linking inhibitor to mix with the silicone polymer precursor coating's surface; and



polymerizing and curing the silicone polymer precursor coating under conditions effective to polymerize and cross-link the silicone polymer precursor coating without cross-linking the surface of the silicone polymer precursor coating contacted with the cross-linking inhibitor, whereby a coated implant having an adhesive surface is formed; and

contacting the adhesive surface of the coated implant with the biological material under conditions effective to attach the medical implant to the biological material.

11. A method according to claim 10, wherein the cross-linking inhibitor is selected from the group consisting of ketones, carboxylic acids, metal salts of carboxylic acids, chlorinated rubbers, butyl rubbers, room-temperature vulcanizing silicone rubbers, sulphur-containing solvents, plasticizers, tin-containing compounds, oxidizing oils, and combinations thereof.

12. A method according to claim 10, wherein said contacting the silicone polymer precursor coating's surface with a cross-linking inhibitor comprises:  
applying the cross-linking inhibitor directly to the silicone polymer precursor coating's surface.

13. A method according to claim 10, wherein the medical implant is a prosthetic appliance.

14. A method according to claim 10, wherein the silicone polymer precursor has a thickness and wherein said agitating mixes the cross-linking inhibitor with the silicone polymer precursor's surface to a depth of from about 10% to about 50% of the thickness of the silicone polymer precursor.

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15. A method for producing a silicone polymeric composition having a drag-reducing surface comprising:

providing a silicone polymer precursor having a surface;

contacting the silicone polymer precursor's surface with a cross-linking inhibitor;

agitating the silicone polymer precursor's surface under conditions effective to cause the cross-linking inhibitor to mix with the silicone polymer precursor's surface; and

polymerizing and curing the silicone polymer precursor under conditions effective to polymerize and cross-link the silicone polymer precursor without cross-linking the surface of the silicone polymer precursor contacted with the cross-linking inhibitor, whereby a silicone polymeric composition having a drag-reducing surface is produced.

16. A method according to claim 15, wherein the cross-linking inhibitor is selected from the group consisting of ketones, carboxylic acids, metal salts of carboxylic acids, chlorinated rubbers, butyl rubbers, room-temperature vulcanizing silicone rubbers, sulphur-containing solvents, plasticizers, tin-containing compounds, oxidizing oils, and combinations thereof.

17. A method according to claim 15 further comprising:

coating a substrate with the silicone polymer precursor prior to said contacting.

18. A method according to claim 17, wherein the substrate is a boat hull, a pipe, or a duct.

19. A method according to claim 17, wherein the silicone polymer precursor forms a coating having a

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thickness of from about 0.1 mm to about 30 mm on the substrate.

20. A method according to claim 17, wherein the substrate is made of a material selected from the group consisting of wood, fiberglass, plastic, metal, glass, and mixtures thereof.

21. A method according to claim 17, wherein the substrate is made of cured silicone.

22. A method according to claim 15, wherein the silicone polymer precursor has a thickness and wherein said agitating mixes the cross-linking inhibitor with the silicone polymer precursor's surface to a depth of from about 10% to about 50% of the thickness of the silicone polymer precursor.

23. A method for reducing boat hull drag comprising:

coating the boat hull with a silicone polymer precursor, wherein the silicone polymer precursor forms a coating on the boat hull, said coating having a surface;

contacting the silicone polymer precursor coating's surface with a cross-linking inhibitor;

agitating the silicone polymer precursor coating's surface under conditions effective to cause the cross-linking inhibitor to mix with the silicone polymer precursor coating's surface; and

polymerizing and curing the silicone polymer precursor coating under conditions effective to polymerize and cross-link the silicone polymer precursor coating without cross-linking the surface of the silicone polymer precursor coating contacted with the cross-linking inhibitor, whereby the drag of the boat hull is reduced.

24. A method for producing a silicone polymeric composition having an adhesive surface comprising:

providing a silicone polymer precursor having a surface;

contacting the silicone polymer precursor's surface with a cross-linking inhibitor comprising a ketone; and

polymerizing and curing the silicone polymer precursor under conditions effective to polymerize and cross-link the silicone polymer precursor without cross-linking the surface of the silicone polymer precursor contacted with the cross-linking inhibitor, whereby a silicone polymeric composition having an adhesive surface is produced.

25. A method according to claim 24, wherein the ketone is selected from the group consisting of acetone, methyl ethyl ketone, diethyl ketone, and combinations thereof.

26. A method according to claim 24, wherein the cross-linking inhibitor comprises acetone.

27. A method according to claim 26, wherein the cross-linking inhibitor further comprises water and a water-soluble amine salt of a fatty acid amide of a hydrolyzed collagen.

28. A method according to claim 27, wherein the water-soluble amine salt of a fatty acid amide of a hydrolyzed collagen is the aminomethylpropanol salt of isostearicamido-hydrolyzed collagen.

29. A method according to claim 26, wherein the cross-linking inhibitor further comprises water and an acid addition salt of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant.

30. A method according to claim 29, wherein the acid addition salt of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant is cocamidopropyl dimethylaminopropionate.

31. A method according to claim 26, wherein the cross-linking inhibitor comprises from about 70 to about 90 wt% acetone, from about 5 to about 17 wt% water, from about 0.01 to about 0.15 wt% of an amine salt of a fatty acid amide of a hydrolyzed collagen, and from about 0.1 to about 0.8 wt% of an acid addition salt of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant.

32. A method for attaching a medical implant to a biological material comprising:

coating the implant with a silicone polymer precursor, wherein the silicone polymer precursor forms a coating on the implant, said coating having a surface;

contacting the silicone polymer precursor coating's surface with a cross-linking inhibitor comprising a ketone;

polymerizing and curing the silicone polymer precursor coating under conditions effective to polymerize and cross-link the silicone polymer precursor coating without cross-linking the surface of the silicone polymer precursor coating contacted with the cross-linking inhibitor, whereby a coated implant having an adhesive surface is formed; and

contacting the adhesive surface of the coated implant with the biological material under conditions effective to attach the medical implant to the biological material.

33. A method according to claim 32, wherein the ketone is selected from the group consisting of

acetone, methyl ethyl ketone, diethyl ketone, and combinations thereof.

34. A method according to claim 32, wherein the cross-linking inhibitor comprises acetone.

35. A method according to claim 34, wherein the cross-linking inhibitor further comprises water and a water-soluble amine salt of a fatty acid amide of a hydrolyzed collagen.

36. A method according to claim 35, wherein the water-soluble amine salt of a fatty acid amide of a hydrolyzed collagen is the aminomethylpropanol salt of isostearicamido-hydrolyzed collagen.

37. A method according to claim 34, wherein the cross-linking inhibitor further comprises water and an acid addition salt of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant.

38. A method according to claim 37, wherein the acid addition salt of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant is cocamidopropyl dimethylaminopropionate.

39. A method according to claim 34, wherein the cross-linking inhibitor comprises from about 70 to about 90 wt% acetone, from about 5 to about 17 wt% water, from about 0.01 to about 0.15 wt% of an amine salt of a fatty acid amide of a hydrolyzed collagen, and from about 0.1 to about 0.8 wt% of an acid addition salt of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant.

40. A method for producing a silicone polymeric composition having a drag-reducing surface comprising:

providing a silicone polymer precursor having a surface;

contacting the silicone polymer precursor's surface with a cross-linking inhibitor comprising a ketone; and

polymerizing and curing the silicone polymer precursor under conditions effective to polymerize and cross-link the silicone polymer precursor without cross-linking the surface of the silicone polymer precursor contacted with the cross-linking inhibitor, whereby a silicone polymeric composition having a drag-reducing surface is produced.

41. A method according to claim 40, wherein the ketone is selected from the group consisting of acetone, methyl ethyl ketone, diethyl ketone, and combinations thereof.

42. A method according to claim 40, wherein the cross-linking inhibitor comprises acetone.

43. A method according to claim 42, wherein the cross-linking inhibitor further comprises water and a water-soluble amine salt of a fatty acid amide of a hydrolyzed collagen.

44. A method according to claim 43, wherein the water-soluble amine salt of a fatty acid amide of a hydrolyzed collagen is the aminomethylpropanol salt of isostearicamido-hydrolyzed collagen.

45. A method according to claim 42, wherein the cross-linking inhibitor further comprises water and an acid addition salt of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant.

46. A method according to claim 45, wherein the acid addition salt of a mono-fatty acid-amido

substituted-trialkylamine cationic surfactant is cocamidopropyl dimethylaminopropionate.

47. A method according to claim 42, wherein the cross-linking inhibitor comprises from about 70 to about 90 wt% acetone, from about 5 to about 17 wt% water, from about 0.01 to about 0.15 wt% of an amine salt of a fatty acid amide of a hydrolyzed collagen, and from about 0.1 to about 0.8 wt% of an acid addition salt of a mono-fatty acid-amido substituted-trialkylamine cationic surfactant.

48. A method for reducing boat hull drag comprising:

coating the boat hull with a silicone polymer precursor, wherein the silicone polymer precursor forms a coating on the boat hull, said coating having a surface;

contacting the silicone polymer precursor coating's surface with a cross-linking inhibitor comprising a ketone; and

polymerizing and curing the silicone polymer precursor coating under conditions effective to polymerize and cross-link the silicone polymer precursor coating without cross-linking the surface of the silicone polymer precursor coating contacted with the cross-linking inhibitor, whereby the drag of the boat hull is reduced.



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US98/15267

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : A61F 2/00; B63B 1/00; C08G 77/08; B32B 9/04, 33/00

US CL : 428/447; 528/15, 17, 18, 31, 32, 34; 523/113, 118; 525/937

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/447; 528/15, 17, 18, 31, 32, 34; 523/113, 118; 525/937

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,623,593 A (BAIER et al.) 18 November 1986, see entire document.	1, 2, 9, 15, 16, 24, 40 ----- 25-31, 41-47

☐

Further documents are listed in the continuation of Box C.

☐

See patent family annex.

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